ESRF	**Experiment title:** X-ray based characterization of nanostructured magnetic molecular switches.	**Experiment number**: HE 3754
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Shifts: 18	**Local contact(s)**: Flora Yakhou	*Received at ESRF:*

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Report:

During our allocated beam time, we studied both the electronic and magnetic properties of two classes of molecular switching systems. The first investigation was in regards to **Spin Crossover (SCO) compounds**, deposited *in situ* as thin films (from sub monolayer to multilayers) via thermal evaporation. The second investigation was into the surface assembling properties from solution of **two valence tautomeric (VT) systems** with different anchoring functional group to the system we investigated during our last beam time (HE-2667). The investigation of both sets of molecules was carried out using XAS and XMCD. By utilizing the unique capabilities of the ID08 beam line it has been possible to track the respective edges through the temperature range of 10K-300K. Also by using the setup that was developed, in collaboration with ESRF technical staff during experiment HE-2544 and HE2667, we were able to irradiate the samples to the meta stable state and track the relaxation back to the ground state, checking for reversibility and reproducibility in order to safely avoid instrumental artifacts and sample degradation. The X-ray induced photo-conversion has been kept to its minimum, thanks to a careful set-up of the optics of the beamline. In this situation, radiation damage induced by x-rays are completely absent from our results. Sub-monolayer coverages of the SCO molecules were prepared on a variety of surfaces. Here the 'Variable Temperature' STM system, provided at ID08, was utilized to characterize the level of coverage on these samples before XAS and XCMD were carried out. The STM was also used to ensure that the surface on which the molecules were evaporated

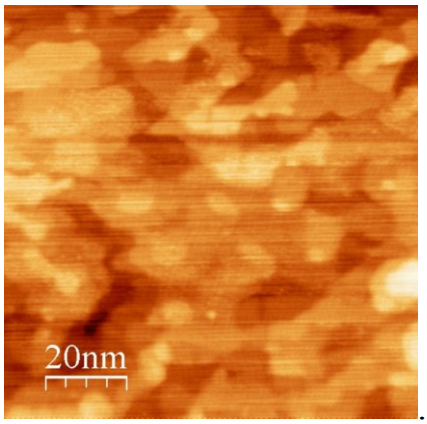


Fig. 1 An image of the Cu_2N surface before evaporation.

were clean and as expected. This was particularly important in regards to Cu_2N, which was prepared inside the UHV system. An image of the Cu_2N surface is seen in Fig 1.

The first stage in the x-ray based investigation of the SCO compounds was to investigate them in the bulk phase. In accordance with magnetometric analysis, a conversion between low spin (LS) state and high spin (HS) state of the *3d* metal center was observed when promoted by temperature variation or light irradiation. Thin films were deposited on to various different substrates *in situ.* Figure 2 shows the XAS data acquired for a sub-monolayer of molecules evaporated onto the Au(111) surface. Here a conversion between high spin and low spin is clearly observed. This investigation included the preparation of a Copper nitride (Cu_2N) thin insulator on the Cu(001) surface to act as a decoupling layer from the metallic substrate.

By investigating the properties of the molecules on these surfaces, and at various different thickness regimes we acquired an insight into the effect of evaporation, surface deposition and cooperative effects of these molecules.

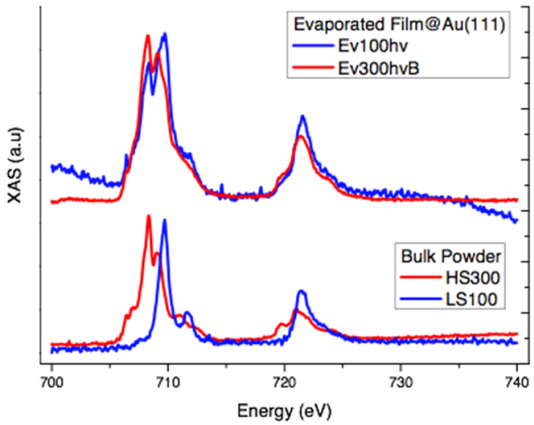
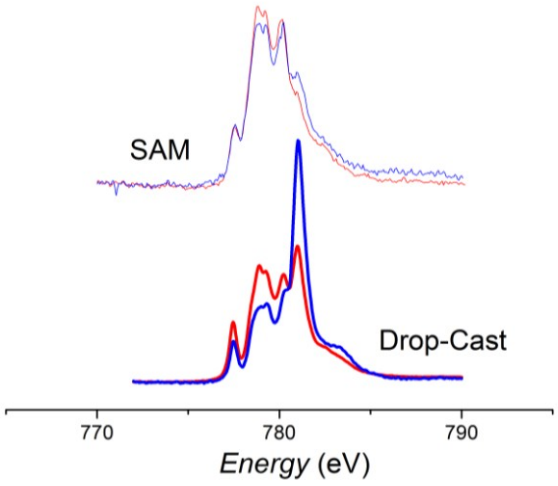


Fig. 2 A comparison of an evaporated SCO film and bulk powder.

The second stage of our investigation involved the comparison between the conversion features of polycrystalline Au(111) self-assembled monolayers and bulk samples, prepared through drop casting technique, of VT compounds. Evidence from XAS (see graph on the right), as well as former *ex situ* X-Ray Photoelectron Spectroscopy analysis,led us to optimize the sample preparation procedure allowing us to be confident that the temperature dependence and irradiation data acquired were of sub-monolayer coverage. SAM data revealed a sensitivity of VT molecule on the distance from the Au surface, showing a strongly reduced VT behavior as 2D deposit.



This comparative study led to an improvement in our understanding of surface confinement effects on these molecules,not only giving us a comprehension of the fundamental science but paving the way for the preparation of new optimized compounds, whose structure may be *a priori* tailored to fully preserve their properties when deposited on surface.

Fig. 3 A comparison of a VT SAM and a bulk film.